Editor-in-Chief

ROBERT J. ANGELICI

Department of Chemistry
Iowa State University

REAGENTS FOR TRANSITION METAL COMPLEX AND ORGANOMETALLIC SYNTHESES

INORGANIC SYNTHESES

Volume 28

A WILEY-INTERSCIENCE PUBLICATION
John Wiley & Sons, Inc.
NEW YORK / CHICHESTER / BRISBANE / TORONTO / SINGAPORE

N490

CONTENTS

Chapter One COMPLEXES WITH WEAKLY COORDINATED LIGANDS

Chapter Five METAL CLUSTER COMPLEXES

Chapter Six CYCLOPENTADIENYL COMPLEXES

2. CARBONYL(η^5-CYCLOPENTADIENYL)-(TETRAFLUOROBORATO)MOLYBDENUM AND -TUNGSTEN COMPLEXES

Submitted by WOLFGANG BECK, KLAUS SCHLOTER, KARLHEINZ SÜNKEL, and GÜNTER URBAN*
Checked by THOMAS FORSCHNER, ALICIA TODARO, and ALAN CUTLER†

A. TRICARBONYL(η^5-CYCLOPENTADIENYL)(TETRAFLUOROBORATO)MOLYBDENUM AND -TUNGSTEN[1a]

An efficient method for the preparation of tetrafluoroborato complexes is hydride abstraction from metal hydrides using triphenylmethylium‡ tetrafluoroborate.[1a] This method has been first reported by Sanders for hydridoruthenium complexes.[2]

$$[Ph_3C][BF_4] + MCp(CO)_3H \rightarrow MCp(CO)_3(FBF_3) + Ph_3CH$$
$$M = Mo, W$$

In a similar way, the hexafluoroarsenato and hexafluoroantimonato complexes $MCp(CO)_3FEF_5$ (M = Mo, W; E = As, Sb) have been prepared from $MCp(CO)_3H$ and $[CPh_3][EF_6]$.[1b]

An alternative method for the preparation of $MCp(CO)_3(FBF_3)$ (M = Mo, W) is protonation of $MCp(CO)_3CH_3$ by $HBF_4 \cdot Et_2O$.[1c]

Procedure

Tritylium tetrafluoroborate is commercially available (Fluka AG) and should be freshly recrystallized from dichloromethane or dichloromethane–ethyl acetate prior to use. The hydrido complexes, $MCp(CO)_3H$[3] should be purified by sublimation or by chromatography (neutral alumina, activity 3, pentane eluant) prior to use. All solvents must be rigorously dried and handled under an inert atmosphere, see the preceding general comments.

A quantity of $Ph_3C[BF_4]$ (0.33 g, 1.0 mmol) is dissolved in 10 mL of CH_2Cl_2 in a 50-mL Schlenk tube, under an inert atmosphere. The solution is

*Institut für Anorganische Chemie der Universität München, Meiserstr. 1,8000 München 2, Federal Republic of Germany.
†Department of Chemistry, Rensselaer Polytechnic Institute, Troy, 12180-3590.
‡ triphenylmethylium = tritylium

cooled to $-40°C$ (using Dry Ice–acetone and a low-temperature thermometer). To this is added $MoCp(CO)_3H$ (Ref. 3) (0.22 g, 0.89 mmol) or $WCp(CO)_3H$ (Ref. 3) (0.30 g, 0.90 mmol). An immediate color change from yellow to purple-red is observed. After stirring for 10 min, 0.2 mL of the solution is syringed into an infrared (IR) solution cell and a spectrum is taken. If a more or less intense band is observed at $\sim 1355\,cm^{-1}$, indicating the presence of unreacted tritylium salt, small amounts of the corresponding hydrides are then added via a spatula. After stirring for 5 min, the IR spectrum is recorded for another solution aliquot. The addition of hydride is repeated until the IR spectrum of the solution shows no band at $1355\,cm^{-1}$. As soon as this equivalence point is reached, a sudden color change from dark red to lilac or violet is observed (see the solution in Section A). If this color change does not occur, the presence of moisture can be suspected. In this case the solution may be used for a reaction with stronger ligands than water, otherwise the preparation has to be tried again.

Two procedures are given for the treatment of the solution in Section A. In the first the solution is cooled down to $-60°C$, and 20 mL of hexane is added. Careful evaporation under vacuum to ~ 20 mL removes most of the CH_2Cl_2. The lilac precipitate is isolated by centrifugation (~ 2 min at 1500 rpm) and decanting off the solution. Hexane (20 mL) is added at $-60°C$ and the suspension is stirred for 10 min. Centrifugation, decanting, and washing are repeated three times. Then the product is dried at $-20°C$ for 8 h on a high-vacuum line (10^{-3} torr).

Alternate Procedure for Treatment of the Solution in Section A

The lilac-colored reaction mixture is transferred into a second Schlenk flask (100 mL) using a double-ended stainless steel cannula. The second flask contains hexane previously cooled to $-78°C$ (Dry Ice–acetone bath). A lilac colored solid precipitates. The solvent is siphoned off and the solid is washed three times with hexane (20 mL) previously cooled to $-78°C$ and transferred into the flask using the double ended cannula technique. The wash solvent is siphoned off and remaining solid is dried under vacuum (10^{-3} torr, oil pump) at $-40°C$ for 8 h. Yields: for $MoCp(CO)_3(FBF_3)$: 282–319 mg (85–96%), for $WCp(CO)_3(FBF_3)$: 357–378 mg (85–90%).

Anal. Calcd. for $C_8H_5BF_4MoO_3$: C, 28.95; H, 1.52. Found: C, 28.27; H, 1.64. Calcd. for $C_8H_5BF_4O_3W$: C, 22.28; H, 1.20. Found: C, 23.63; H, 1.39.

*Properties**

*See Section B.

B. DICARBONYL(η^5-CYCLOPENTADIENYL)(TETRAFLUOROBORATO)(TRIPHENYLPHOSPHINE)MOLYBDENUM AND -TUNGSTEN, $MCp(CO)_2(PPh_3)(FBF_3)$(M = Mo, W)[4]

Substitution of a CO group by a phosphine ligand makes the metal center electron-richer and therefore less Lewis acidic. This weakens the coordination of the $[BF_4]^-$ ion. In addition, steric interactions with the phosphine ligands, the possibility of cis–trans isomerism in the complexes with "four-legged piano stool" geometry,[5] and the introduction of the ^{31}P nucleus as another sensitive NMR probe make this variation of the synthesis described in Section A, an interesting field of further investigation. The preparation described here for the PPh_3 compounds, can also be used with other PR_3 ligands such as PMe_3, PEt_3, $P(OPh)_3$, or $\frac{1}{2}$(dppe)[dppe = 1,2-ethanediyl-bis(diphenylphosphine)].†

Dicarbonyl(η^5-cyclopentadienyl)hydrido(triphenylphosphine) molybdenum and -tungsten

$$MCp(CO)_3H + PPh_3 \rightarrow MCp(CO)_2(PPh_3)H + CO$$

$$M = Mo, W$$

Monophosphine substituted carbonylcyclopentadienylhydrido complexes of molybdenum and tungsten have been obtained by protonation of the anions $[MCp(CO)_2(PR_3)]^-$[6], or by substitution of CO with phosphines in the hydrides $MH(CO)_3Cp$.[7] The straightforward synthesis of the hydrides $MH(CO)_3Cp$(M = Mo, W)[3] makes the latter procedure preferable, at least for PPh_3, $P(OPh)_3$, PMe_3, and PEt_3, where fast reactions and good yields can always be obtained. For the analogous syntheses of PMe_3 or PEt_3 substituted hydrides, special precautions for handling these highly toxic, malodorous, and highly inflammable phosphines must be taken.[8]

Procedure

A quantity of freshly sublimed $MCp(CO)_3H$ (0.49 g, M = Mo or 0.66 g, M = W, each 2.0 mmol) is dissolved in 15 mL of hexane at room temperature in a 100-mL Schlenk flask. To this is added PPh_3 (0.58 g, 2.1 mmol) under vigorous stirring. The Schlenk tube is then connected to a mercury bubbler and a stream of argon (0.5 L min^{-1}) is passed over the solution for 2 h (it is not necessary to bubble the argon through the solution). Soon a white precipitate

†Commonly known as 1,2-bis(diphenylphosphino)ethane.

forms, which is isolated by filtration under argon and washed twice with 5 mL of hexane. The product is dried at room temperature for 6 h *in vacuo*. It may be recrystallized from CH_2Cl_2–hexane. Yields: $MoCp(CO)_2(PPh_3)H$, 625 mg, 65%; $WCp(CO)_2(PPh_3)H$, 636 mg (56%).

Properties

The hydrides $MCp(CO)_2(PPh_3)H$ are yellowish-white powders. They are air stable for several minutes exposure as solids, however, for extended storage they should be kept under argon. IR spectra (in CH_2Cl_2): $\nu_{CO} = 1936$, 1856 cm^{-1} (Mo); 1923, 1835 cm^{-1} (W); ^1H NMR [in CD_2Cl_2 (Mo), $CDCl_3$ (W)]: $\delta_{C_5H_5} = 5.08$ (Mo); 5.10 ppm (W); $\delta_{M-H} = -5.56$ (Mo), -7.06 ppm (W), "doublets" $^2J_{(^{31}P^1H)_{av}} = 47$ Hz (Mo), 55 Hz (W); ^{31}P NMR (in CD_2Cl_2): $\delta_{PPh_3} = 74.3$ (Mo), 40.9 ppm (W) (relative to H_3PO_4). A fast equilibrium between the cis and trans isomers[5] leads to averaging of the signals and coupling constants at room temperature. Both isomers can be distinguished by low-temperature ^1H NMR [δ_{Mo-H}: -5.33 d and -6.14 d; $^2J_{^{31}P^1H} = 64$ and 21.4 Hz; δ_{W-H}: -6.90d, -7.36d, $^2J_{^{31}P^1H} = 65$ and 22 Hz].

The analogous PMe_3 and PEt_3 containing hydrides tend to form oils and decompose quickly on contact with air; the tungsten compounds are more stable than the molybdenum analogs. Their spectral properties are similar to those of the PPh_3 compounds. The best yields are obtained with the $P(OPh)_3$ ligand, which leads exclusively to the stable cis isomers.[5]

Dicarbonyl(η^5-cyclopentadienyl)(tetrafluoroborato)(triphenylphosphine)-molybdenum and -tungsten[4]

$$[Ph_3C][BF_4] + MCp(CO)_2(PPh_3)H \rightarrow MCp(CO)_2(PPh_3)(FBF_3) + Ph_3CH$$

$$M = Mo, W$$

Procedure

Generally, the same guidelines as described in Section A have to be followed. A quantity of $MoCp(CO)_2(PPh_3)H$ (0.45 g, 0.94 mmol) or $WCp(CO)_2(PPh_3)H$ (0.55 g, 0.97 mmol) is added to a solution of $[Ph_3C][BF_4]$ (0.33 g, 1.00 mmol) in 10 mL CH_2Cl_2 at $-40°C$ contained in a Schlenk flask (100 mL) equipped with a magnetic stirring bar. The mixture is stirred for 20 min, after which an IR spectrum is recorded of an aliquot (0.2 mL) to inspect the intensity of the band at 1355 cm^{-1}. Small amounts of the hydride

are added until the IR spectrum, recorded at 5-min intervals shows no band at 1355 cm^{-1}. Usually, a lilac precipitate forms before the equivalence point is reached. The equivalence point is again indicated by a lilac color of the solution. Complete precipitation of the product is obtained by addition of 20 mL of hexane at −60°C, or by transfer of the complete reaction mixture to another Schlenk flask containing the hexane cooled to −60°C (see the procedure in Section A). Isolation of the product is the same as described in Section A. Yields: $MoCp(CO)_2(PPh_3)(FBF_3)\cdot 2CH_2Cl_2$ 632 mg. (86%); $WCp(CO)_2(PPh_3)(FBF_3)$ 556 mg (85%).

Anal. Calcd. for $C_{25}H_{20}BF_4MoO_2P\cdot 2CH_2Cl_2$: C, 44.1; H, 3.29. Found: C, 45.0; H, 3.32.

Properties

All tetrafluoroborato complexes are very sensitive to moisture. Schlenk tubes used for storage therefore have to be heated to 400°C or more under vacuum for several hours; O-ring stopcocks or similar grease-free stopcocks are superior to the usual ground-glass stopcocks. Although the phosphine containing BF_4 complexes are thermally more stable than the unsubstituted compounds, storage at temperatures below −25°C under Ar is recommended for all these compounds. They dissolve in CH_2Cl_2 and $CHCl_3$ below −40°C without decomposition, while solvents with donor properties like acetone or acetonitrile dissolve these complexes under substitution of tetrafluoroborato ligands by the solvent to give ionic complexes, for example, $[MoCp(CO)_3(acetone)][BF_4]$. They can be characterized by their IR spectra in the region from 1200 to 700 cm^{-1} and by their low-temperature ^{19}F and, where appropriate, ^{31}P NMR spectra.[9]

TABLE I. Spectroscopic Data of $MoCp(CO)_2L(FBF_3)$

	L = CO
IR: ν_{CO}	2071, 1988 cm^{-1} (in CH_2Cl_2)
ν_{11BF}	1130, 884, 722 cm^{-1} (in Nujol)
^{19}F NMR:[a]	−155d ($MoFBF_3$), −370q ($MoFBF_3$), 95 Hz ($^2J_{F-F}$)
	L = PPh_3
IR: ν_{CO}	1991, 1903 cm^{-1} (in CH_2Cl_2)
ν_{11BF}	1119, 901, 732 cm^{-1} (in Nujol)
^{19}F NMR:[a]	−155d ($MoFBF_3$), −344q, −391q ($MoFBF_3$), 90 Hz ($^2J_{F-F}$)

[a] δ in ppm, relative to $CFCl_3$, in CD_2Cl_2, −80°C.

TABLE II. Spectroscopic Data of $WCp(CO)_2L(FBF_3)$

L = CO
IR: ν_{CO} = 2067, 1975 cm^{-1} (in CH_2Cl_2)
ν_{11BF} = 1149, 874, 704 cm^{-1} (in Nujol)
^{19}F NMR:[a] −153d ($WFBF_3$), −394q ($WFBF_3$), 99 Hz ($^2J_{F-F}$)
L = PPh_3
IR: ν_{CO} = 1988, 1963, 1877 cm^{-1} (in Nujol)
ν_{11BF} = 1148, 887, 720 cm^{-1} (in Nujol)
^{19}F NMR:[b] −156d ($WFBF_3$), −371q ($WFBF_3$), 98 Hz ($^2J_{F-F}$)

[a] δ in ppm, relative to $CFCl_3$, in CD_2Cl_2, −52°C.
[b] δ in ppm, relative to $CFCl_3$, in CD_2Cl_2, −80°C.

Coordination of the BF_4 ion lowers the T_d symmetry of $[BF_4]^-$ and makes the fluorine atoms nonequivalent. Therefore the IR spectra show three instead of one ν_{11B-F} absorptions[1,4] (Tables I and II); the low-temperature ^{19}F NMR spectra[9] show two distinct fluorine resonances, a high-field quartet (which may be split by coupling to the phosphorus in the PR_3 substituted compounds and a doublet at lower field, close to the resonance of free $[BF_4]^-$;[13] the ^{31}P NMR spectrum shows at low temperature a pseudodoublet, produced by coupling with the coordinated fluorine (Tables I and II). Compounds $MoCp(CO)_2(PR_3)(FBF_3)$ are obtained as cis and trans isomers. In $WCp(CO)_2[P(OPh)_3](FBF_3)$ total isomerization from the pure cis hydride to the pure *trans*-BF_4 compound could be followed via NMR.[9]

Reactions of Tetrafluoroborato Complexes with Ethylene, Diphenylacetylene, and Acetone

General Remarks

The tetrafluoroborate ligand of these highly reactive complexes can be easily substituted by a series of N, O, P, and S σ donors[1a,4,10,11] and π donors (see Sections C–F).

As described in Sections A and B, a lilac solution of the corresponding tetrafluoroborato complex is prepared at −30°C in 10 mL of CH_2Cl_2. Complete reaction of the tritylium salt is verified by checking for the disappearance of the 1355 cm^{-1} absorption in the IR spectrum of the solution. This solution is used for the following reactions without isolation of the tetrafluoroborato complex.

C. TRICARBONYL(η^5-CYCLOPENTADIENYL)(η^2-ETHENE)-MOLYBDENUM(1+) TETRAFLUOROBORATE(1−)[1a]

$$MoCp(CO)_3(FBF_3) + C_2H_4 \rightarrow [MoCp(CO)_3(\eta^2\text{-}C_2H_4)][BF_4]$$

The title compound can be obtained in three ways. One method starts from $Mo(C_5H_5)(CO)_3Cl$, which is reacted with C_2H_4 at a pressure of 70 bar in the presence of $AlCl_3$ and consecutive precipitation with ammonium salt.[12] A second method involves β-hydride abstraction from the ethyl group in $MoCp(CO)_3(C_2H_5)$ by $[Ph_3C][BF_4]$.[13] The third method, described here, has the advantage of mild reaction conditions and a good overall yield. Analogous complexes with other olefins have been prepared similarly.[4]

Procedure

Ethylene (1 bar), dried over P_2O_5, is bubbled through a vigorously stirred lilac solution of $MoCp(CO)_3(FBF_3)$ (1 mmol) in CH_2Cl_2 in a Schlenk flask (50 mL) cooled to −30°C. With continuous ethylene bubbling, the cooling bath is removed and the flask is permitted to warm up to +20°C over a 4-h period. The flow of ethylene is then stopped, and the reaction mixture stirred under argon for another 30 min. The yellow precipitate is isolated by centrifugation or filtration under Ar. After washing four times with 5 mL of CH_2Cl_2, the product is dried 1 h at +40°C on a high-vacuum line. It may be recrystallized from acetone–diethyl ether. Yield: 282 mg (79%).

Properties

The compound decomposes on heating at 102–108°C. Infrared spectra (in Nujol): $\nu_{CO} = 2104$, 2053, 2001 cm^{-1}; ^1H NMR (acetone-d_6) $\delta = 6.35$ ppm (C_5H_5).

D. CARBONYL(η^5-CYCLOPENTADIENYL)BIS(DIPHENYL-ACETYLENE)MOLYBDENUM(1+) TETRAFLUORO-BORATE(1−)[1a]

$$MoCp(CO)_3(FBF_3) + 2PhCCPh \rightarrow [MoCp(CO)(PhCCPh)_2][BF_4] + 2CO$$

Other syntheses of cationic bis(alkyne) complexes of molybdenum and tungsten of the same type include $AgBF_4$ oxidation of the dimer $[MoCp(CO)_3]_2$ in CH_2Cl_2 in the presence of diphenylacetylene or several

other alkynes.[14] Protonation of $MoCp(CO)_3CH_3$ with CF_3COOH and consecutive addition of 2-butyne in acetonitrile, followed by precipitation with a methanolic solution of $[NH_4][PF_6]$ gives the corresponding 2-butyne complex.[15] Refluxing a solution of $MoCp(CO)_3Cl$ with $(HOCH_2)CC(CH_2OH)$ leads to an analogous compound.[16] The method described here uses very mild conditions and can be applied also for other alkynes, like 2-butyne or acetylene.[17]

Procedure

Diphenylacetylene (535 mg, 3.0 mmol) is added to a lilac solution of $MoCp(CO)_3(FBF_3)$ (1 mmol in 10 mL CH_2Cl_2, prepared as described above) at $-30°C$ under vigorous stirring in a Schlenk flask (50 mL) equipped with a magnetic stirring bar. The flask is connected to a mercury bubbler and flushed by a constant flow of argon or nitrogen gas. After 30 min, the gas flow is stopped and the cooling bath removed. Stirring is continued for 4 days at room temperature, over which time a yellow precipitate is formed. Diethyl ether (20 mL) is added and the yellowish-red suspension is filtered under argon. The residue on the frit is extracted three times with 10 mL of CH_2Cl_2. The combined extracts are evaporated to 5 mL, to which is added diethyl ether (20 mL). The orange-yellow precipitate is isolated by centrifugation or filtration under argon, washed three times with 10-mL aliquots of diethyl ether, and then dried for 1 h *in vacuo* at 40°C. The product may be recrystallized from CH_2Cl_2–pentane. Yield: 235 mg (37%).

Anal. Calcd. for $C_{34}H_{25}BF_4MoO$: C, 64.58; H, 3.99. Found: C, 63.98; H, 4.09.

Properties

The yellow compound is soluble in polar solvents such as CH_2Cl_2, acetone, or acetonitrile. Although prolonged exposure to air leads to decomposition, the compound can be handled in air for short periods of time. Its IR spectrum in Nujol shows one $\nu_{^{12}CO}$ vibration at 2088 cm^{-1} and a weak $\nu_{^{13}CO}$ band at 2040 cm^{-1}. Also a weak absorption at 1741 cm^{-1} occurs, which may be due to the $\nu_{C=C}$ band of the coordinated alkyne. The ^1H NMR spectrum in CH_2Cl_2 has a sharp singlet for the C_2H_5 protons at $\delta = 6.20$ ppm, besides the broad resonance of the phenyl protons of the diphenylacetylene. Interestingly, KBr pellets of the compound several hours after initially formed show a bathochromic shift of the ν_{CO} band, which is also observed with other cationic alkyne complexes.[17]

E. CARBONYL(η^5-CYCLOPENTADIENYL)(DIPHENYLACETYLENE)(TRIPHENYLPHOSPHINE)MOLYBDENUM(1+) TETRAFLUOROBORATE(1−)[18]

$$MoCp(CO)_2(PPh_3)(FBF_3) + PhCCPh \rightarrow$$
$$[MoCp(CO)(PPh_3)(PhCCPh)][BF_4] + CO$$

Green and coworkers[19] prepared the title compound and other related monoalkyne complexes by reaction of the corresponding bis(alkyne) complex with triphenylphosphine (or other phosphines) in good yields. The method described here works for several alkynes, for example, 2-butyne or phenylacetylene, and also for phosphines, for example, PEt_3 or $P(OPh)_3$.

Procedure

Diphenylacetylene (1.78 g, 10.0 mmol) is added to a magnetically stirred lilac suspension of $MoCp(CO)_2(PPh_3)(FBF_3)$ (1.0 mmol in 10 mL of CH_2Cl_2, as described previously) in a Schlenk flask (50 mL) cooled to −30°C. The flask is connected to a mercury bubbler and purged with argon for 15 min. The gas flow is stopped and the cooling bath is allowed to warm up to room temperature. Stirring is continued for 2 days, during which time the flask is purged several times with argon to remove the carbon monoxide evolved in the reaction. Then hexane (20 mL) is added. Stirring is continued for another day at ambient temperature, after which the dark green suspension is filtered under argon. The residue on the filter is washed four times with 15-mL aliquots of hexane and then dried 3 h under vacuum at 25°C. Yield: 408 mg (57%).

Anal. Calcd. for $C_{38}H_{30}BF_4MoOP$: C, 63.7; H, 4.22. Found: C, 62.8; H, 4.15.

Properties

The title compound is soluble in polar organic solvents, for example, acetone, acetonitrile, or dichloromethane. Although storing under inert gas is recommended, no decomposition can be observed when handled as a solid in air for short periods of time. IR (in CH_2Cl_2): $\nu_{^{12}CO} = 1987\ cm^{-1}$; ^1H NMR (CD_2Cl_2): $\delta_{C_5H_5} = 5.77$ ppm, $\delta_{C_6H_5,P(C_6H_5)_3}$ 8–7 ppm; ^{31}P NMR (in CD_2Cl_2) $\delta_{PPh_3} = 54.8$ ppm.

The crystal structure of this compound shows a slightly elongated C≡C bond of the alkyne and the usual deviation from linearity at the two carbon atoms of the triple bond.[18,19].

F. (ACETONE)(TRICARBONYL)(η^5-CYCLOPENTADIENYL)-MOLYBDENUM(1+) AND -TUNGSTEN(1+) TETRAFLUOROBORATE(1−)[1a,10]

$$MCp(CO)_3(FBF_3) + (CH_3)_2CO \rightarrow [MCp(CO)_3OC(CH_3)_2][BF_4]$$

$$M = Mo,\ W$$

Procedure

A lilac solution of the tetrafluoroborato complex $MCp(CO)_3(FBF_3)$, M = Mo or W (1 mmol in 10 mL of CH_2Cl_2) is prepared as indicated above in a Schlenk flask (50 mL) and cooled to −30°C. To this is added acetone (0.1 mL, 1.38 mmol). An immediate color change to red occurs, and stirring is continued for 3 h. Hexane (15 mL) is then added. The solution is cooled to −78°C (Dry Ice) and stored overnight, giving a dark red precipitate. This is isolated by centrifugation and washed twice with 19 mL of hexane at 0°C. Alternatively, the supernatant solution may be removed by a stainless steel cannula fitted with a sintered-glass frit. The solids are washed with two aliquots of cold (0°C) hexane (19 mL), each removed by use of the stainless steel cannula fitted with the glass frit. The product is then dried for 6 h at 0°C on a high-vacuum line. Yield: $MoCp(CO)_3(OC(CH_3)_2)(BF_4)$ 350 mg (90%); $WCp(CO)_3[OC(CH_3)_2](BF_4)$ 420 mg (88%).

Anal. Calcd. for $C_{11}H_{11}BF_4MoO_4$: C, 33.88; H, 2.84. Found: C, 33.87; H, 2.85. Calcd. for $C_{11}H_{11}BF_4O_4W$: C, 27.65; H, 2.32. Found: C, 26.90; H, 2.45.

Similar acetone complexes can also be prepared from the PPh_3 containing tetrafluoroborate complexes.

Properties

Solutions of the compounds in CH_2Cl_2 or acetone decompose at 20°C within a short time, especially when traces of water are present. The solid compounds can be stored under argon at −30°C for several weeks without decomposition.

IR (CH_2Cl_2): $\nu_{CO} = 2072$, 1987 cm^{-1} (Mo) IR (in Nujol): $\nu_{CO} = 2050$, 1930 cm^{-1} (W); $\nu_{M-O=C} = 1660$ cm^{-1} (Mo), 1640 cm^{-1} (W). ^1H NMR (in CD_2Cl_2): $\delta_{C_5H_5} = 6.11$ (Mo), 6.19 ppm (W); $\delta_{CH_3} = 2.39$ (Mo), 2.43 ppm (W).

References

1. (a) W. Beck and K. Schloter, *Z. Naturforsch. Teil B*, **33,** 1214 (1978); (b) K. Sünkel, U. Nagel, and W. Beck, *J. Organomet. Chem.*, **251,** 227 (1983); (c) M. Appel, K. Schloter, J. Heidrich, and W. Beck, *J. Organomet. Chem.* **322,** 77 (1987).
2. J. R. Sanders, *J. Chem. Soc. Dalton Trans.*, **1972,** 1333.
3. (a) R. B. King and F. G. A. Stone, *Inorg. Synth.*, **7,** 107 (1963). E. O. Fischer, *Inorg. Synth.* **7,** 136 (1963); (b) R. B. King, *Organometallic Syntheses*, Vol. 1, Academic Press, New York, 1965, p. 156; (c) W. P. Fehlhammer, W. A. Herrmann, and G. K. Öfele, in *Handbuch der Präparativen Anorganischen Chemie*, Vol. 2, 3th ed., F. Enke Verlag, Stuttgart, 1981.
4. K. Sünkel, H. Ernst, and W. Beck, *Z. Naturforsch. Teil B*, **36,** 474 (1980).
5. J. W. Faller and A. S. Anderson, *J. Am. Chem. Soc.*, **92,** 5852 (1970).
6. (a) A. R. Manning, *J. Chem. Soc. A*, **1968,** 651; (b) M. J. Mays and S. M. Pearson, *J. Chem. Soc. A*, **1968,** 2291.
7. (a) A. Bainbridge, P. J. Craig, and M. Green, *J. Chem. Soc. A*, **1968,** 2715; (b) P. Kalck, R. Pince, R. Poilblanc, and J. Roussel, *J. Organomet. Chem.*, **24,** 445 (1970).
8. R. T. Markham, E. A. Dietz, Jr., and D. R. Martin, *Inorg. Synth.*, **16,** 153 (1976).
9. K. Sünkel, G. Urban, and W. Beck, *J. Organomet. Chem.*, **252,** 187 (1983); M. Appel and W. Beck, *J. Organomet. Chem.*, **319,** C1 (1987).
10. K. Sünkel, G. Urban, and W. Beck, *J. Organomet. Chem.*, **290,** 231 (1985).
11. K. Schloter and W. Beck, *Z. Naturforsch. Teil B*, **35,** 985 (1980); G. Urban, K. Sünkel, and W. Beck, *J. Organomet. Chem.*, **290,** 329 (1985).
12. E. O. Fischer and K. Fichtel, *Chem. Ber.*, **94,** 1200 (1961).
13. M. Cousins and M. L. H. Green, *J. Chem. Soc.*, **1963,** 889.
14. M. Bottrill and M. Green, *J. Chem. Soc. Dalton Trans.*, **1977,** 2365.
15. P. L. Watson and R. G. Bergman, *J. Am. Chem. Soc.*, **102,** 2698 (1980).
16. J. W. Faller and H. H. Murray, *J. Organomet. Chem.*, **172,** 171 (1979).
17. K. Schloter, K. Sünkel and W. Beck, unpublished results.
18. K. Sünkel, U. Nagel, and W. Beck, *J. Organomet. Chem.*, **222,** 251 (1981).
19. S. R. Allen, P. K. Baker, S. G. Barnes, M. Green, L. Trollope, L. Manojlovic-Muir, and K. W. Muir, *J. Chem. Soc. Dalton Trans.*, **1981,** 873.